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Title: ASTM D03 Workshop: Developing a Hydrogen Contamination Detector Analyzer

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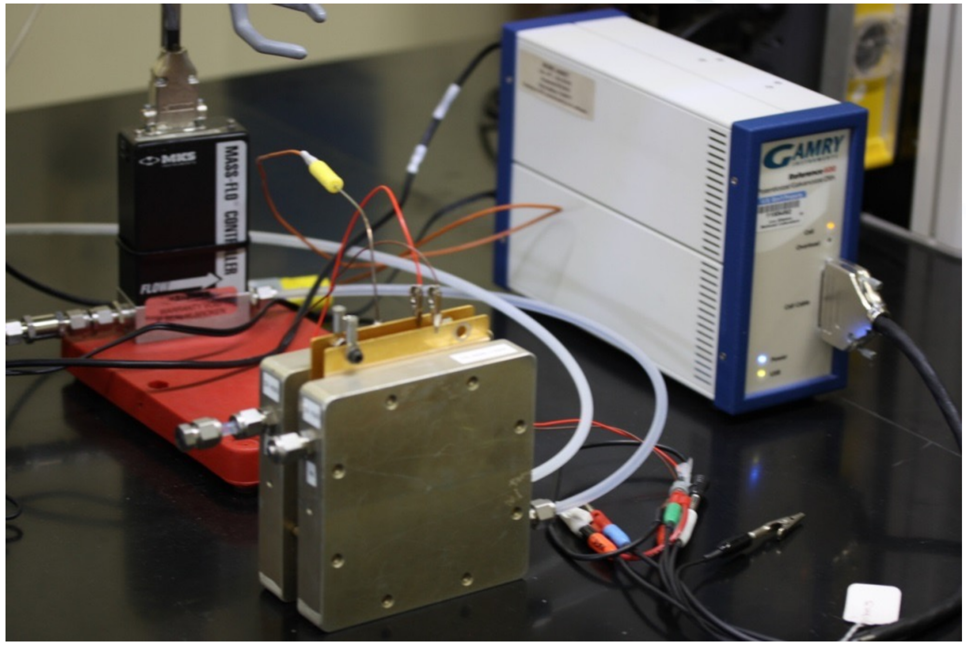
ASTM D03 Workshop: Developing a Hydrogen Contamination Detector Analyzer



Team(alphabetically):

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Dec 8, 2021

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HCD Background

Problem:

Non-hydrogen constituents in the fuel steam can cause irreversible damage to FC systems and therefore should be avoided.

Objectives:

1. Develop a low-cost fast response device (analyzer) to measure impurities in a dry hydrogen fuel stream at or above the SAE J2719 levels.

Analyzer Targets:

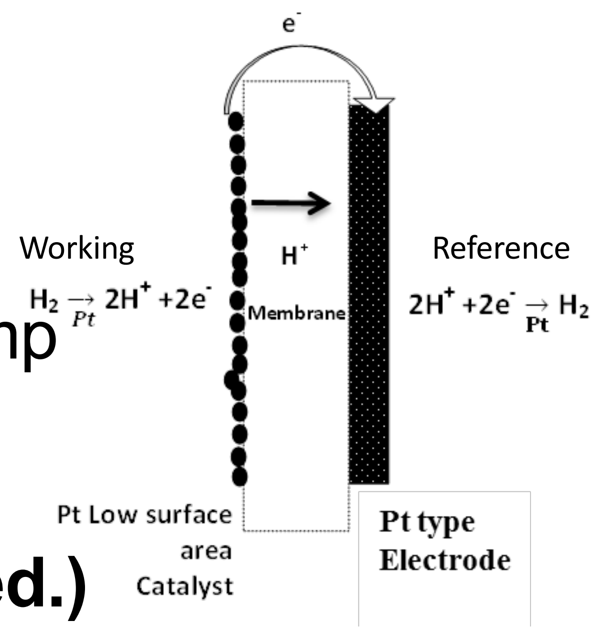
SAE J2719 Limit	Filling Time
200 ppb CO	~ 5 min

2. Develop understanding of working mechanism and improve analyzer by **identifying the best materials and their configuration (Timeline of improvements)**

3. Test the analyzer in real-world environments

Approach

- Use a **mini fuel cell** in/at the hydrogen stream to detect impurities that can be harmful to the fuel cell stack
- **No oxygen or water** available at the filling station, challenges:
    1. Provide hydration via a ***Wicking Scheme (Offline Analysis)***
    2. Operate w/o H_20 inside fuel stream at High P & low T **(*Inline Analysis)***
- HCD operates as an electrochemical H_2 pump using a MEA-type configuration. Measure pumping current before, during and after contaminant exposure**. (No Oxygen required.)**

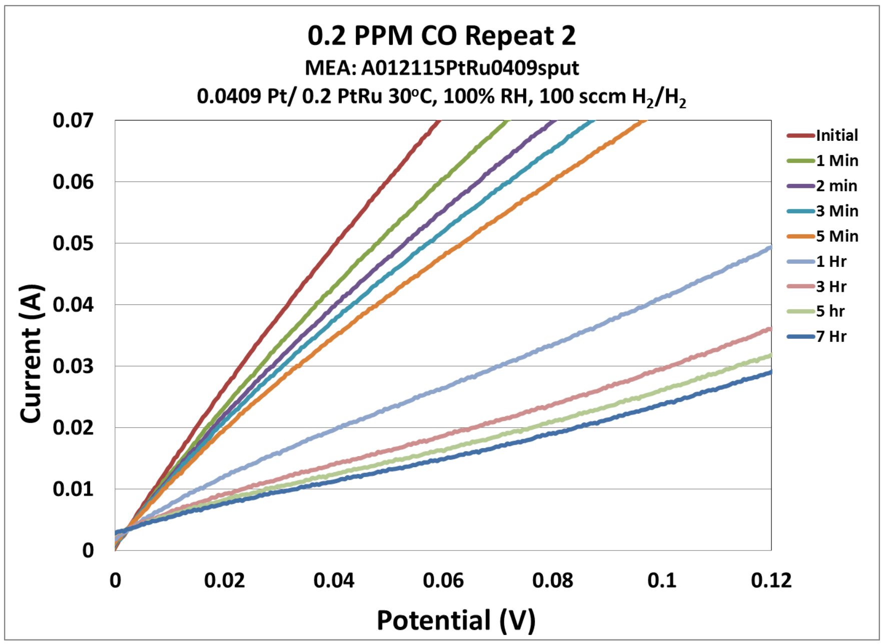


Identifying & Testing Desirable Materials (FY15)

Proof-of-Concept Shown

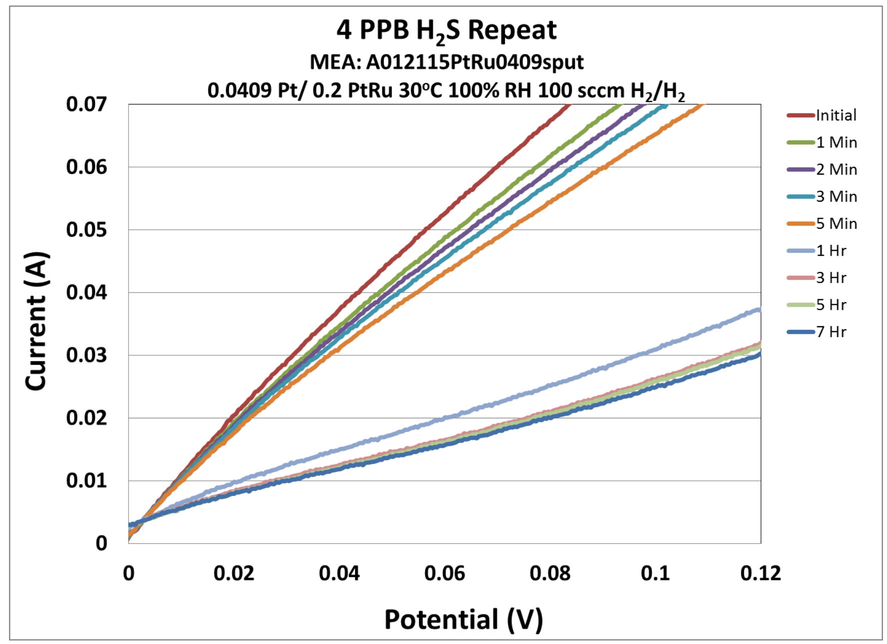
Reference Electrode: Tolerant and Stable

- **Pt: 30 wt %, Ru: 23.3 wt %,** High surface area to mass ratio 3.5nm particle size
- Carbon black with 5% Nafion® painted decals



Working Electrode: Durable and Sensitive

Sputtered low loaded electrode provides stable Pt particle sizes and high sensitivity to impurities.



Desired response times obtained for both CO and H_2S at the SAE level!

Response time < 5 minutes!!!

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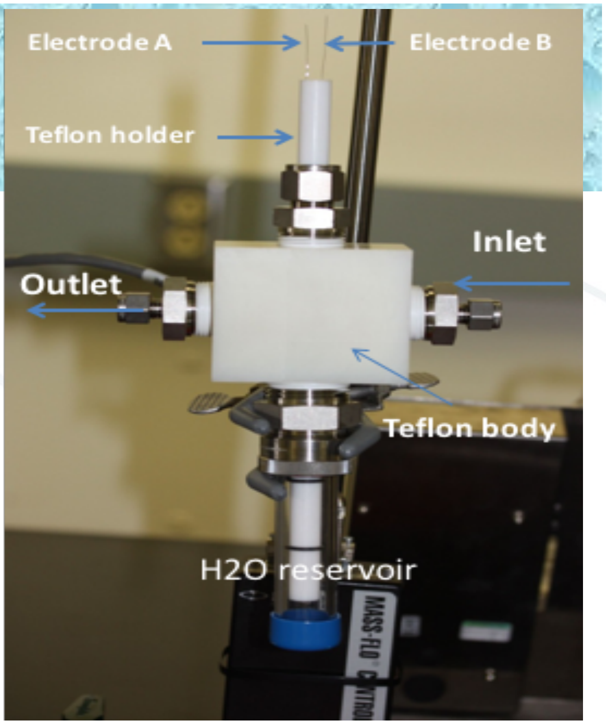
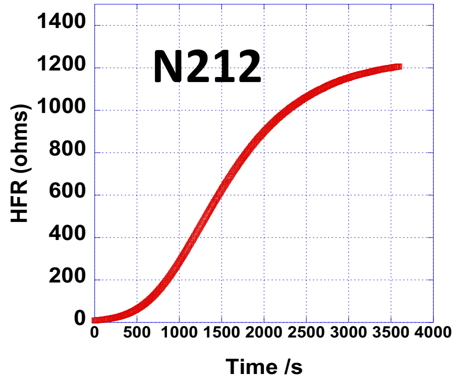
Developing the Prototype(FY16)

- **Membrane Hydration Challenging**: Identifying conditions needed for constant membrane humidification
  - Confirm by measuring HFR w/varying flow and membrane thickness
- Determine a **fuel flow-rate** that will not compromise sensitivity or response time



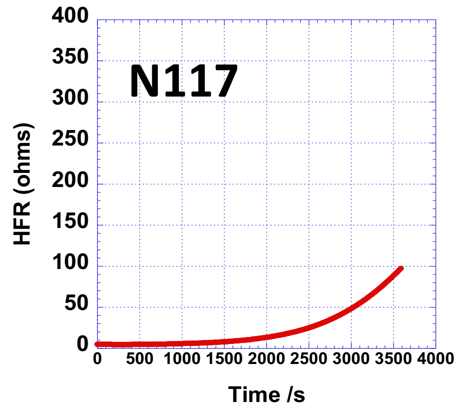
Membrane Saturated

N212 membrane HFR at 50kHz - 1L/min N2
HFR_Membranehumidification8



N212, HFR increases in the presence dry gas flow

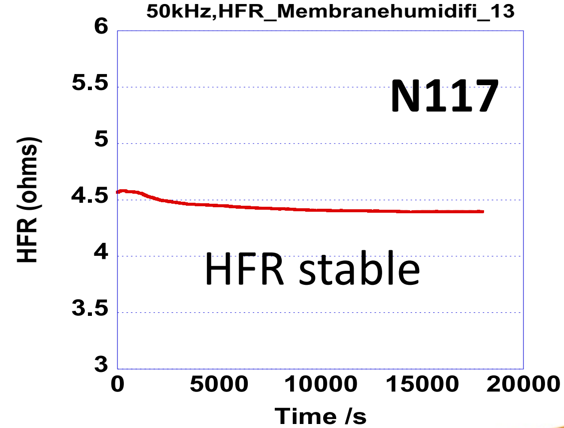
N117 membrane HFR at 50kHz - 1L/min N2
HFR_Membranehumidification8



N117 maintains hydration longer

Re-designed hydration scheme

N117 with GDLs
400 ml/min 6%H2/Ar bal ran overnight continuous
5 hr stability HFR next day
50kHz,HFR_Membranehumidifi_13



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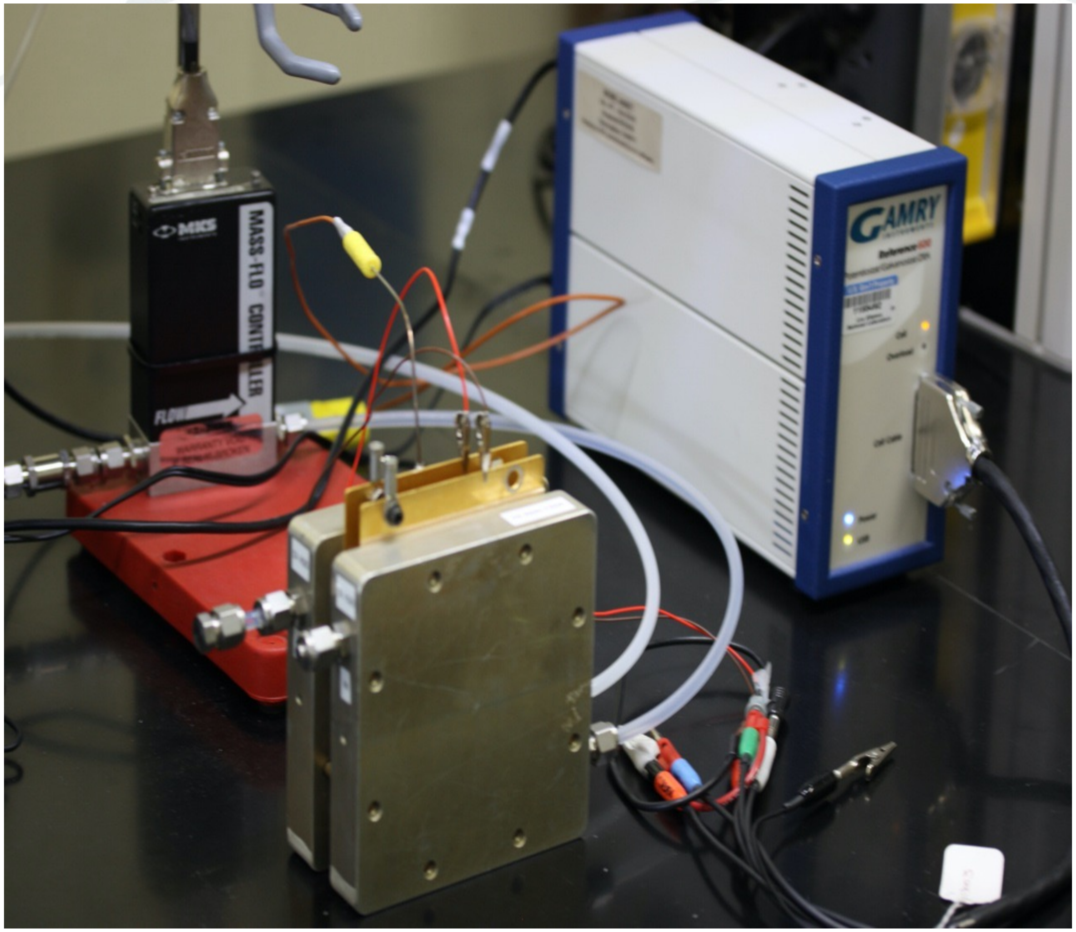
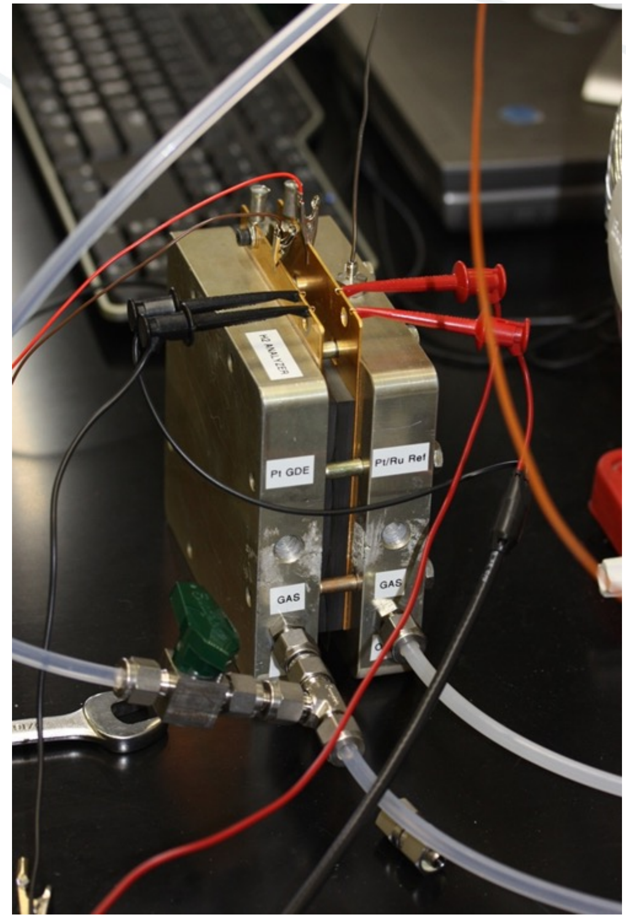
Prototype Developed (FY16)

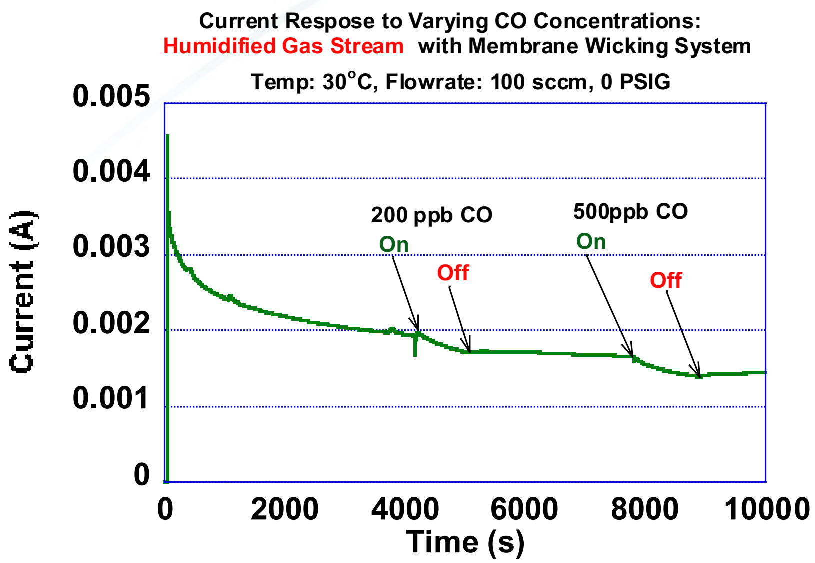


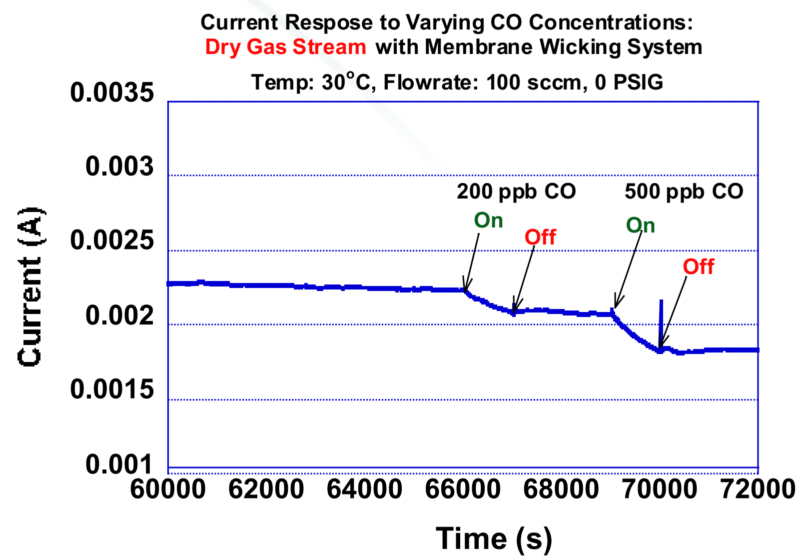


- Newly designed prototype developed using standard FC hardware
- IP protection initiated for membrane hydration system

Improved Humidification (FY17)

0.039 mg Pt/cm^2; Low Pt, 0.2 mg Pt/Ru (RE) T: 30^{o}C, P: 0 psig, Flowrate: 100 sccm





- Baseline experiments
- Gases were externally humidified
- 25 BC GDL
- CO exposure shows clear response

- Dry gases with wicking humidification system
- GDL changed to a less hydrophobic material
- More stable than 'Baseline'
- Responds to 200 and 500 ppb CO

No natural recovery observed !!!

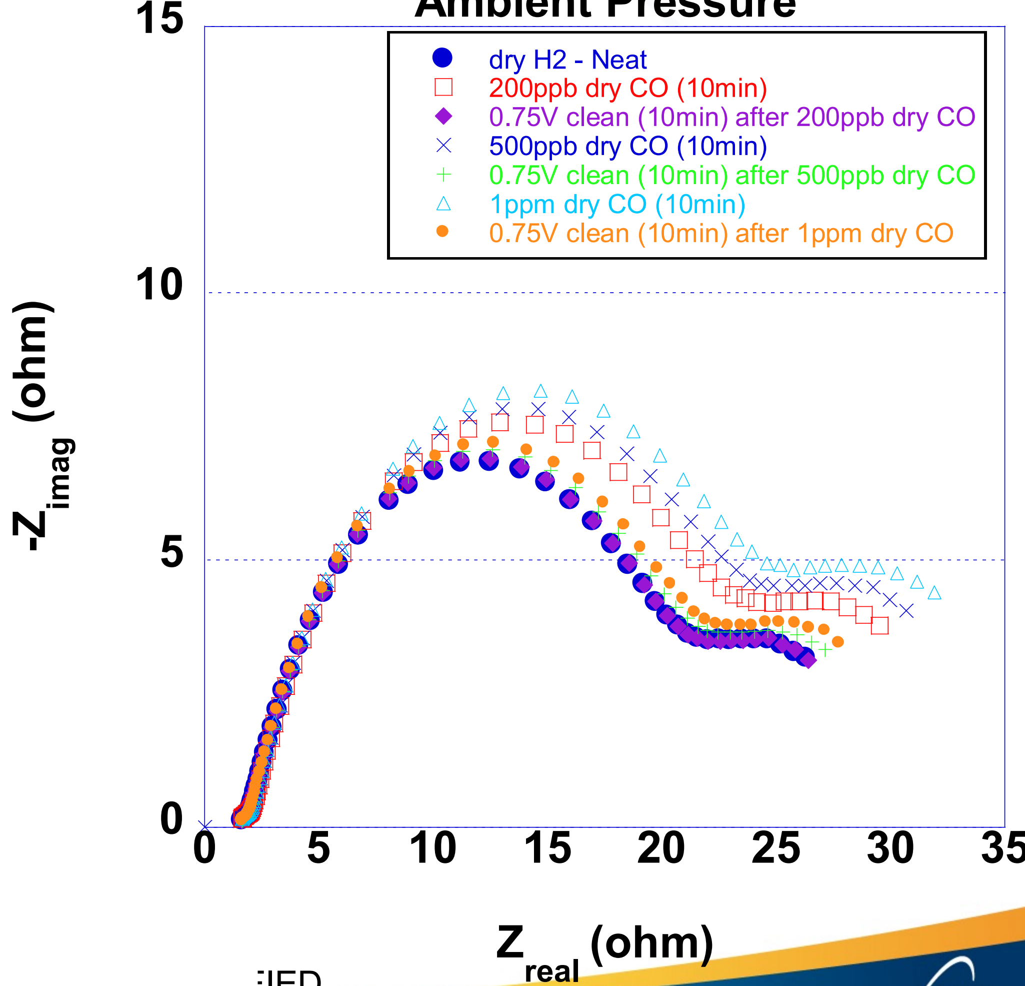
Applying a Clean-Up Strategy (FY17)

How to reset the analyzer?

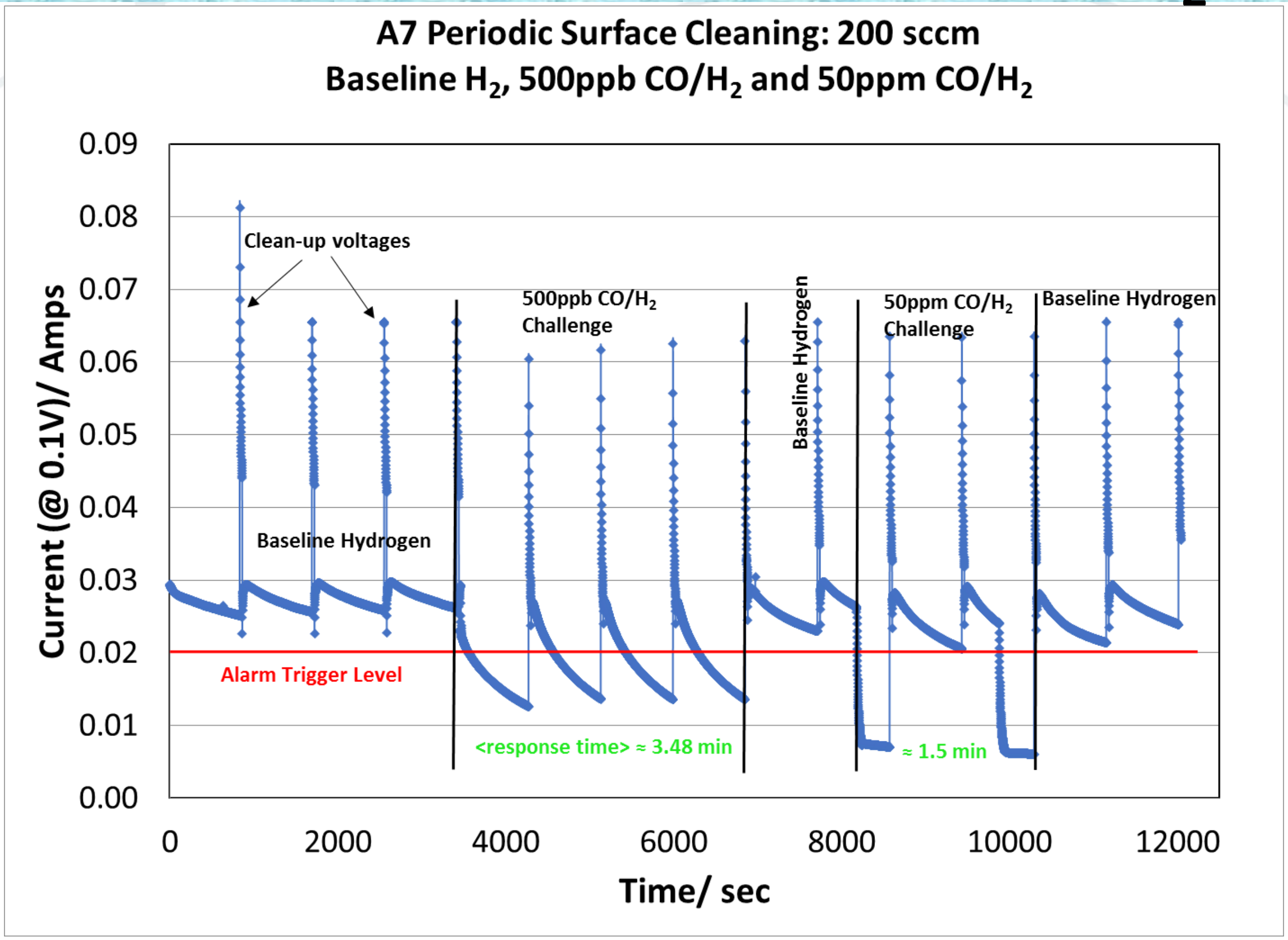
- Applied 0.75V as a 'Clean-Up' Method
- Analyzer reset after 200 ppb CO
- **Recovery not complete at highest concentrations**

Imp Spectras for Varying CO Concentrations:
10 min at 0.1 V, Ionomer Impact

Temp: 30°C, Flowrate: 100 sccm, Ambient Pressure



Proposed Operating Mode Demonstrated (FY18) 200 sccm H_2



Ave. Response Time:

500ppb CO: **3.48 min**

50ppm CO: **1.5 min**

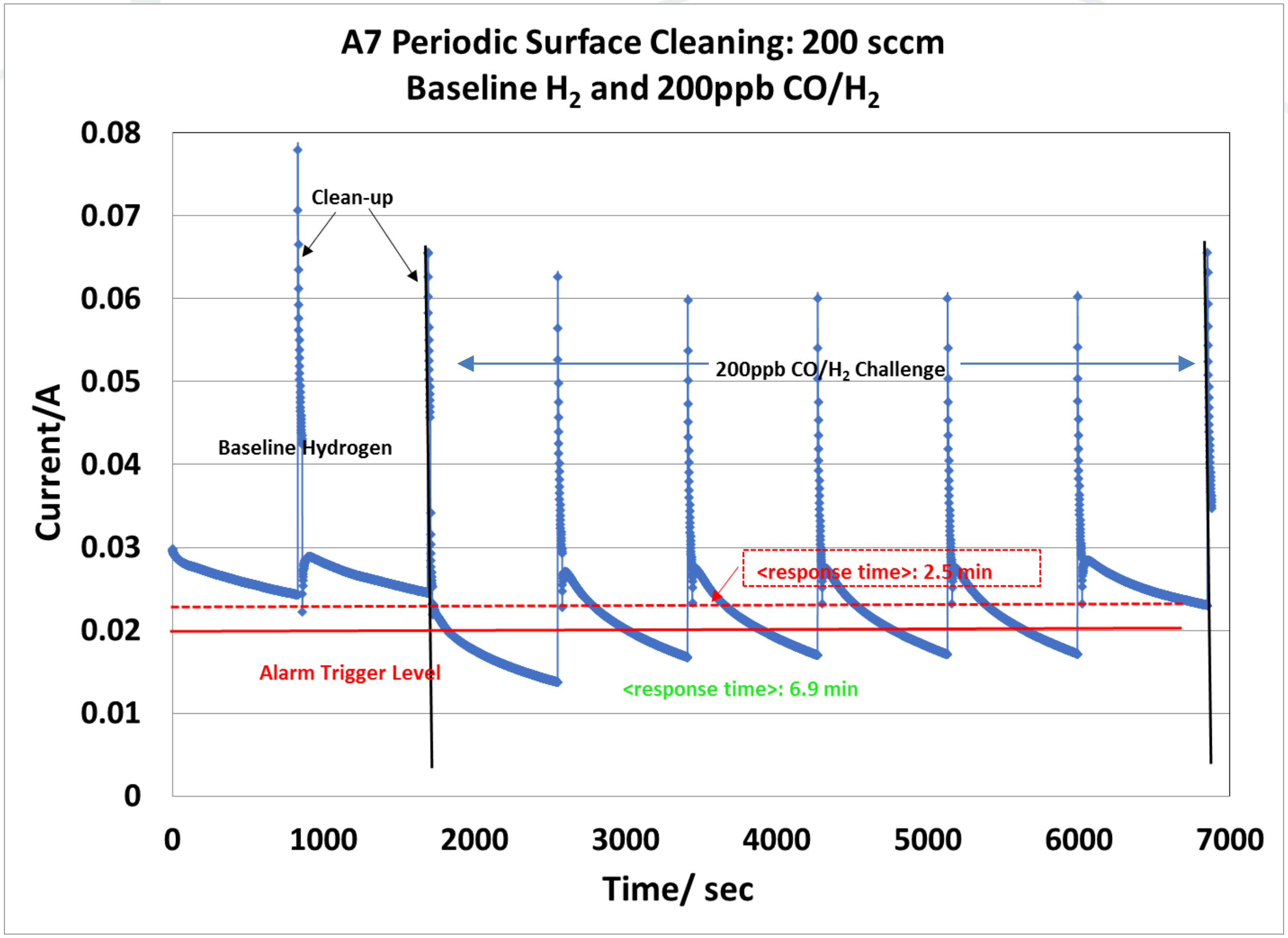
•Apply periodic cleanup voltages (1.5V for 30s) and measure current during 15 minute recovery intervals. (**Current kept in operating window)**

•**Alarm trigger level can be set (e.g. 20 mA).**

•**Analyzer current loss tracks with CO concentration.**

- Higher H_2 flow rate demonstrated using identical clean-up strategy.
- **Response time< 5 min (goal)**.
- Total current loss similar for 100(not shown) and 200 sccm flow rates

Proposed Operating Mode Demonstrated (FY18) SAE 2719 Level



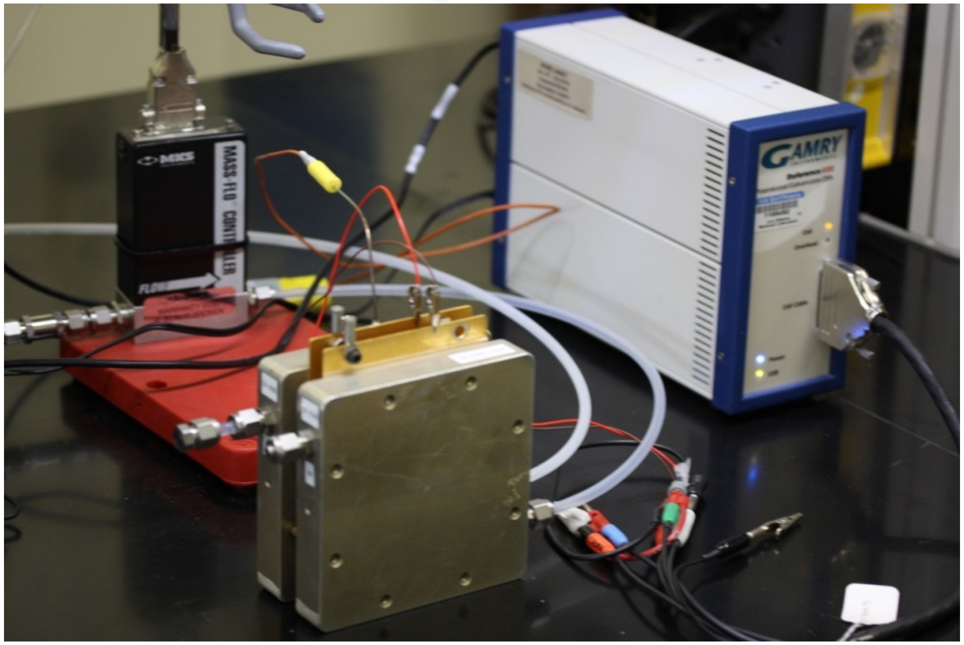
Ave Response Time: **6.9 min**

Adjusted Trigger Level
Ave Response Time: **2.5 min**

- Sensitivity to 200ppb CO demonstrated.
- Analyzer response time > 5 min. **(goal not met)**
- **Adjusting trigger level allows 200ppb CO to alert in 2.5 min.**

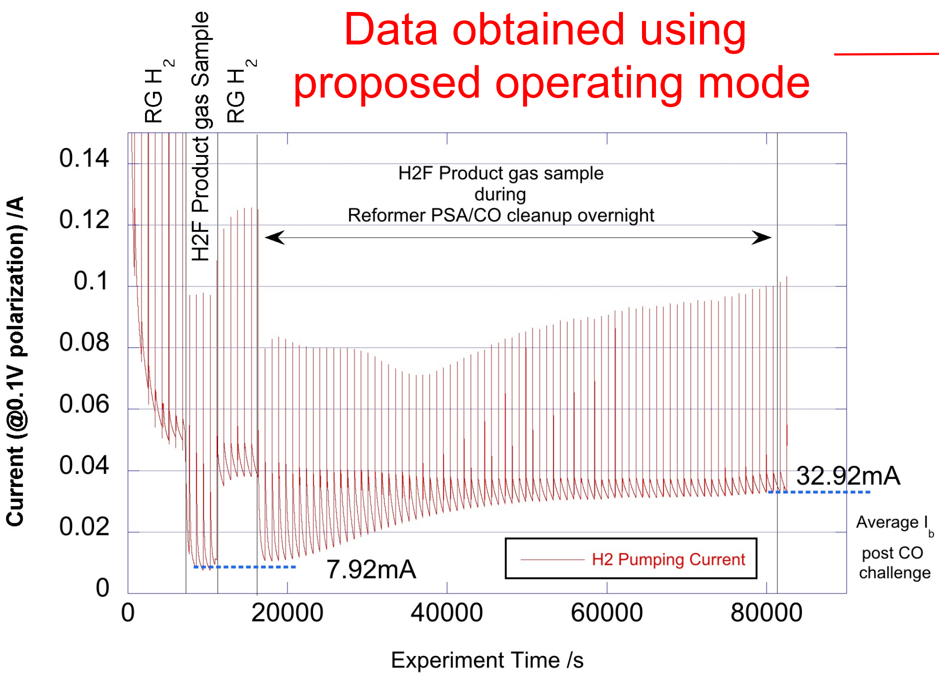
Testing in Real-World Conditions (FY19)

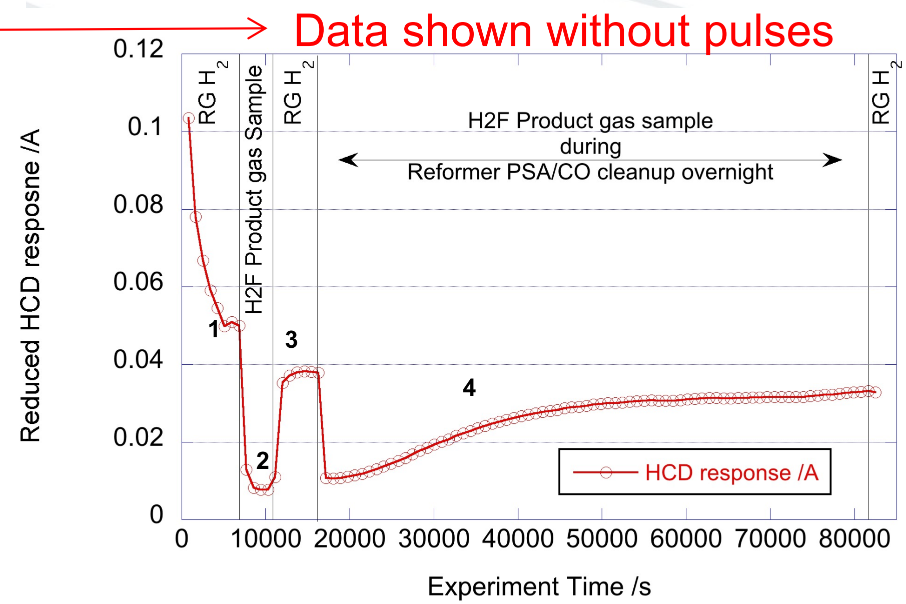
- Operation in the field may presents challenges not captured with laboratory testing. For example,
    - Sensitivity in the field
    - Maintaining stability
    - Analyzer cell lifetime
    - Durability issues
    - Local temp swings



Analyzer set-up for testing in the field

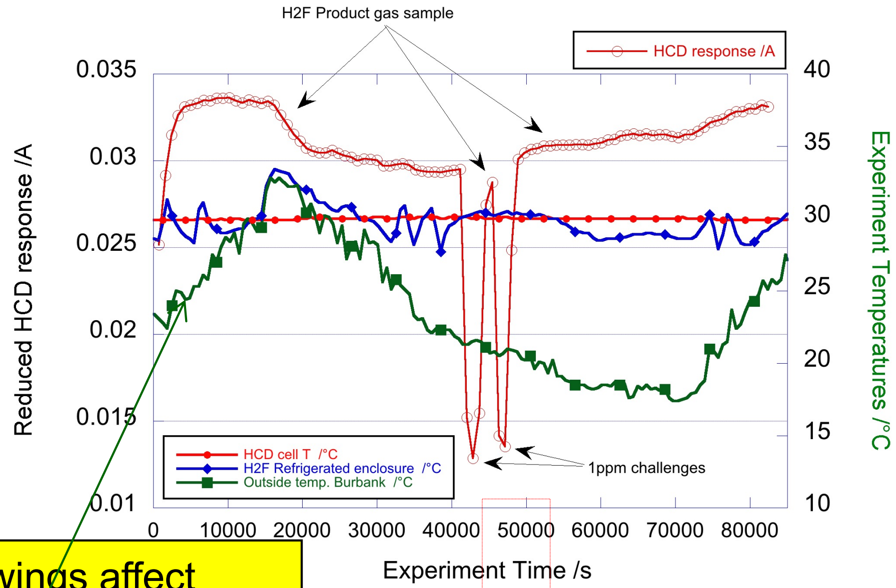
Field Trials (FY19)

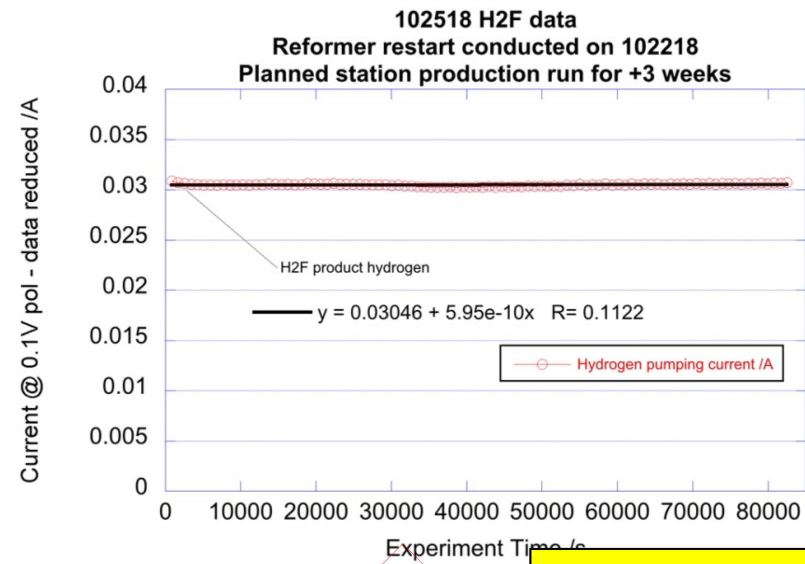




- Operating mode: 0.1V hold with periodic cleaning pulse applied, 1.5V. **(left graph)**
- Data shown without pulses **(right graph)** :
    1. Research grade (RG) H_2 sampled until reformer began.
    2. CO present during reformer start-up evident by sharp current decay.
    3. Performance recovers after returning to RG H_2
    4. Current increases as product gas becomes cleaner.

Impact of Ambient Temp (FY19)

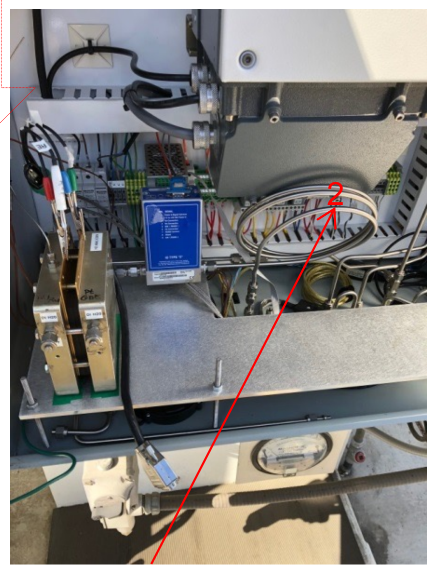




T swings affect baseline stability

Modifications provided stable baseline.

Insulation applied



Gas sample loop

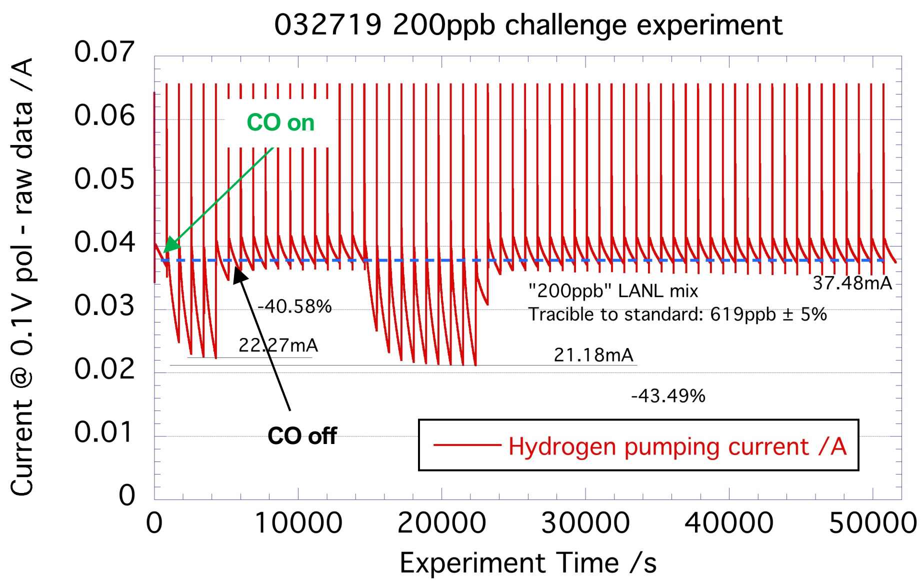
Modifications made to mitigate impact of local temp:

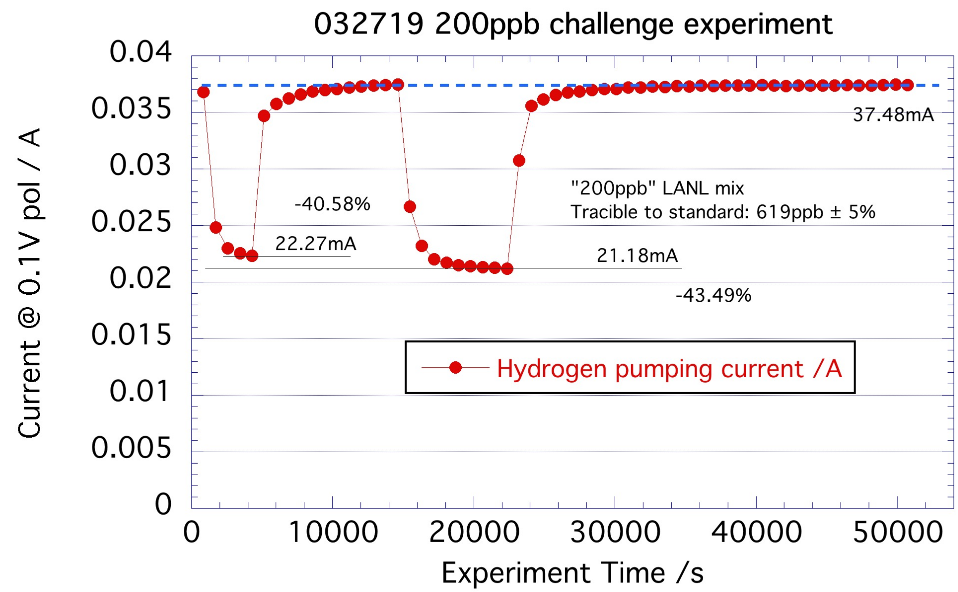
1. Insulation applied to exterior manifold and supply gas lines.
2. Internal sample loop installed to allow sample gas temp more time to equilibrate.

Field Results (FY19): SAE/ISO CO Level

Offline Analysis

- New enclosure for HCD testing equipment
- Certified 200ppb bottles of CO/H_2 mixtures are <u>not commercially available.</u>
- A low pressure bottle (<25psi) of test gas was prepared using a NIST traceable standard.
- Raw data(left) plot shows measured current value (0.1V polarization) with clean-up voltage (1.5V) and without on the right.

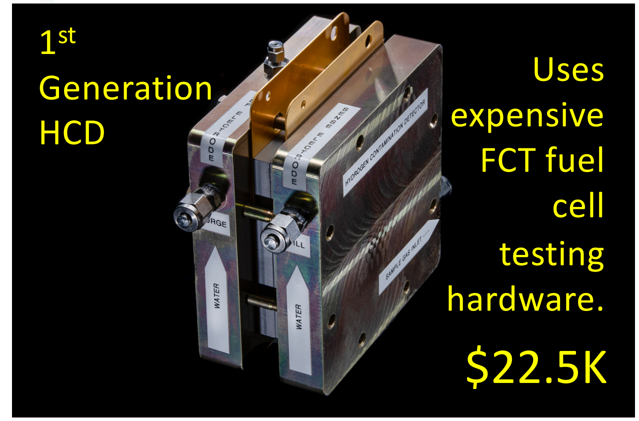




- HCD successfully detected 200ppb CO outside of laboratory conditions.
- A large current loss is observed when 200ppb CO is injected into the H2F hydrogen stream.

New HCD and Components for Low-Cost System

- **Present retail cost, not including labor, recently estimated to be $3215/system.**
- **Compare to previous system field-tested at Burbank H2F which cost $22,500 not including the cost of the required refrigerated instrument cabinet.**



✓Machined Ti HCD plates: $400/set

✓Membrane/GDLs/GDE WE/CE: ~ $50ea

✓Peltier thermal module: $175

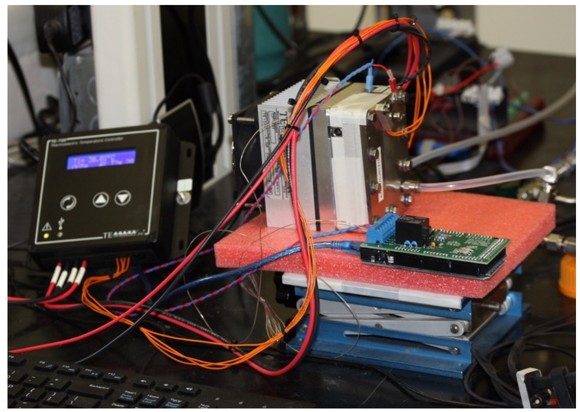
✓Peltier controller: $750

✓Machined Al adapter plate: ~ $240ea

✓VI Controls HCD controller: $1500ea

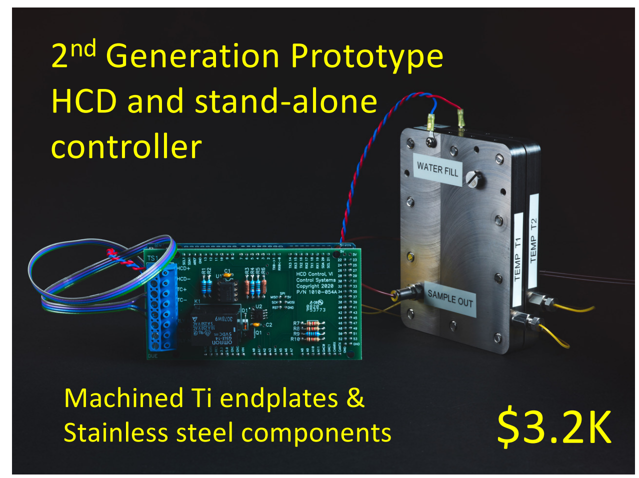
✓Misc: ~$100/unit

- Relay and MOSFET added for external control of H2Frontier E-stop system to shut down H_2 delivery to storage if CO rises above 200 ppb from methane reformer system. Arduino based system



Gen 2: Peltier thermal module controls temperature for flexible deployment

Gen 1 Field test at Burbank: HCD and Gamry unit were placed inside refrigerated enclosure already onsite.



Validation and Verification Testing HCD

- HCD test results provided by **Skyre** reproduce the performance characteristics and testing results obtained at LANL and at the H2Frontier hydrogen fueling station.
- Low cost (Gen2) HCD performance comparable to Gen1

Results from Skyre (CRADA final report)

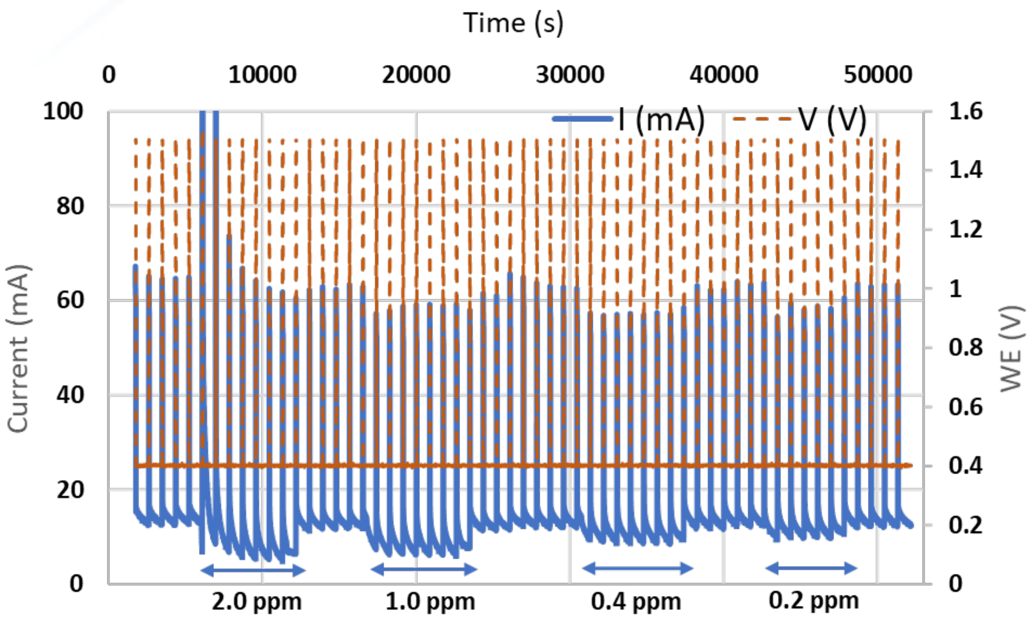


Figure 6. Evaluation of 2nd Gen HCD functionality – CA sensing-cleaning cycles for the verification of contamination-recovery in 2.0, 1.0, 0.4 & 0.2 ppm CO in H_2

2nd Gen HCD performance in 0.2, 0.4,1.0, and 2.0 ppm CO

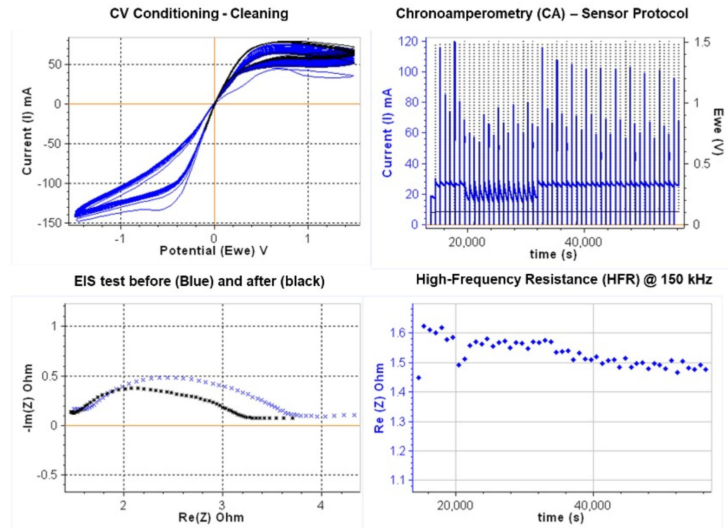


Figure 5. First-Generation HCD's contamination-recovery in 0.2 PPM CO in Zero H_2

1st Gen HCD performance in 200ppb CO

Contaminant Concentration vs. HCD test parameters	Zero-Grade H_2	2 ppm CO in H_2	1 ppm CO in H_2	0.4 ppm CO in H_2	0.2 ppm CO in H_2
Baseline Current (mA)	30	30	25	28	28
Current Upon Contamination (mA)	N/A	12	12	20	22
% of Contamination	0%	60%	52%	29%	21%
Recovery of Baseline	Yes	Yes	Yes	Yes	Yes
Cell Resistance (Ohm)	1.2-1.3	1.5-1.7	1.3-1.5	1.5-1.7	1.4-1.7

Table 1. 1st Gen HCD evaluation parameters for different CO-concentration in Zero-grade H_2 gas

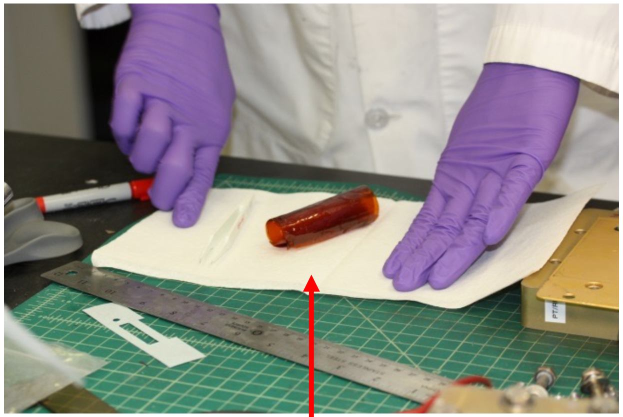
1st Gen HCD performance in 0.2, 0.4,1.0, and 2.0 ppm CO

Developing an Inline HCD

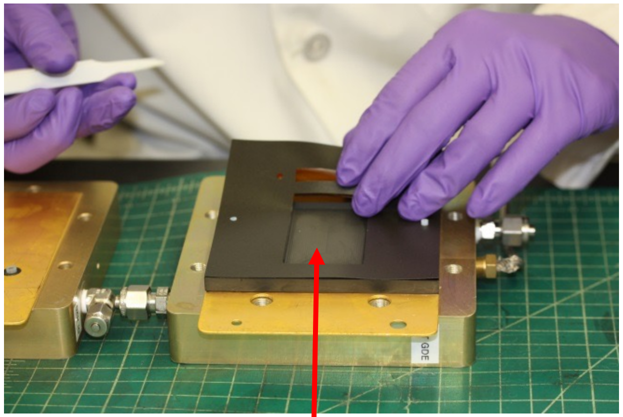
Approach

Replace Nafion® with a proton-conducting thermoplastic membrane that will not require water to function.

Polybenzimidazole (PBI) based HCD work

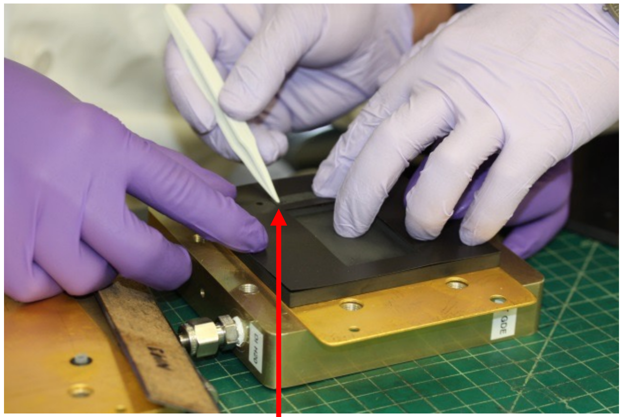


PBI membranes prepared by LANL researchers with 5, 10, and 15% H_3PO_4.



Same HCD hardware used but humidification scheme not used.

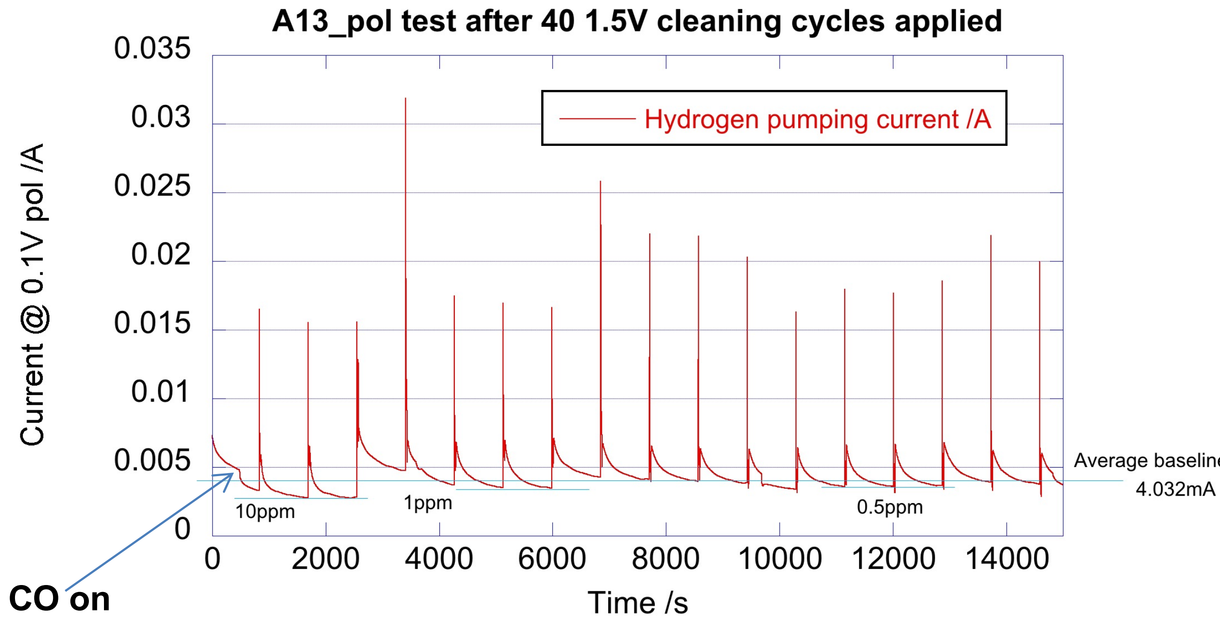
Excess H_3PO_4 applied to GDE/GDL before assembly.

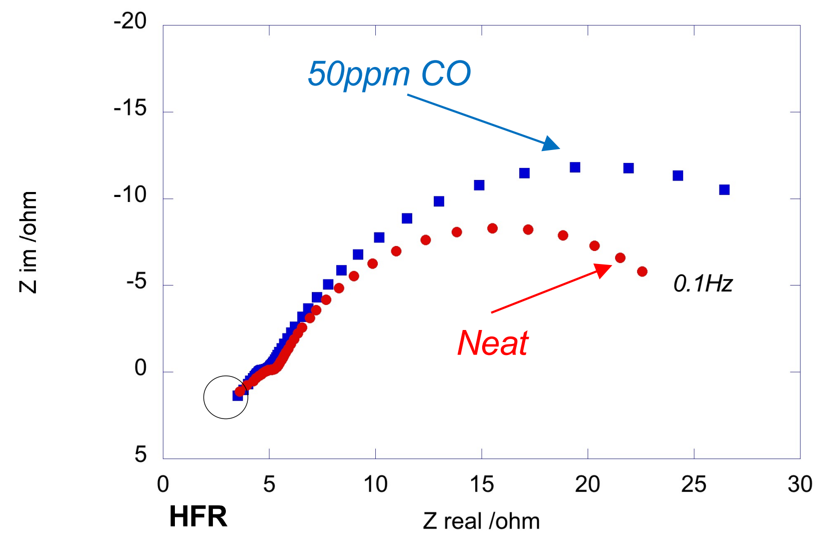


Same sputtered, low-Pt loaded GDL used / PtRu CE. With or without ionomer.

HCD: Initial PBI Results

- Use identical operating mode
- Current response to higher concentration CO similar to Nafion® HCD.
- Impedance spectra: an increase in charge transfer resistance is indicative of catalyst poisoning (i.e. CO adsorption)
- No response to CO at the SAE level
- Cell conditioning different from Nafion® based HCD.





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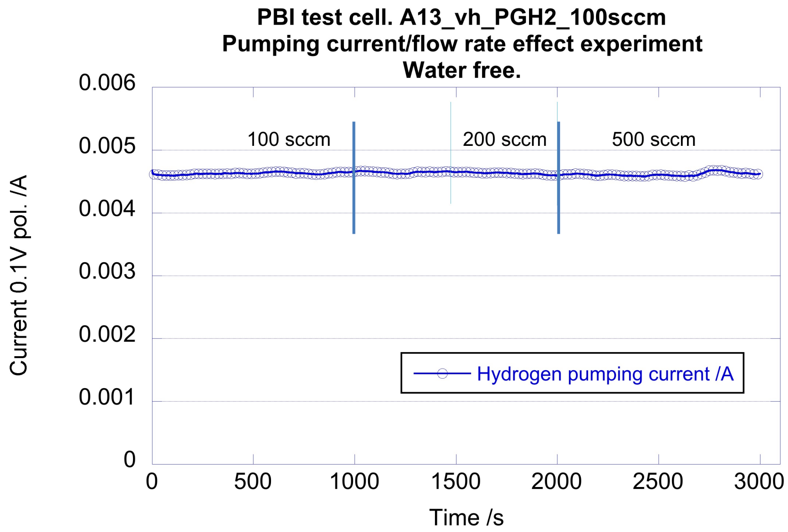
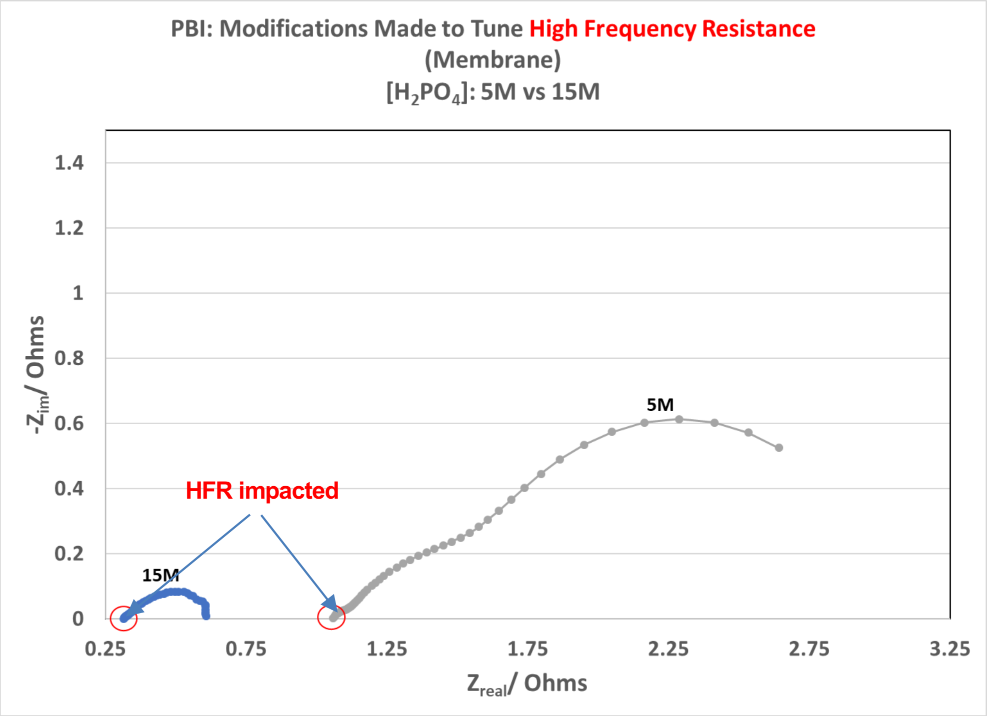
PBI-based HCD Flowrate Impact:

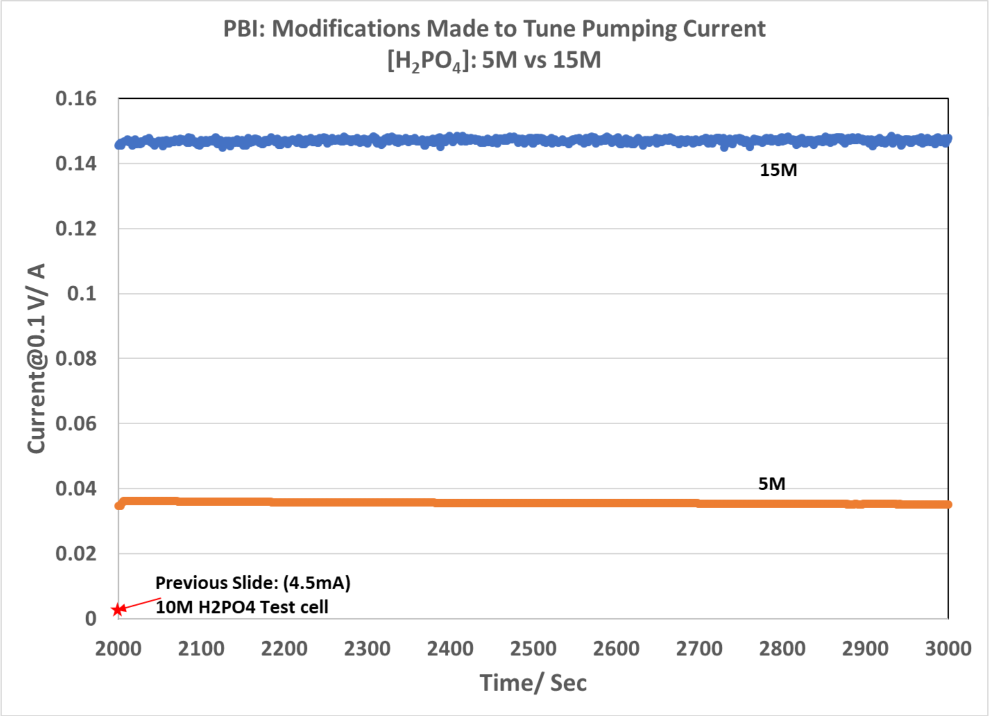


- *No water reservoir*
- *Flow independent baseline current*
- *Initial performance lower*

PBI-based HCD operated in completely water-free, dry H_2 stream. The current response remained constant even after a 5X increase in flowrate.

PBI HCD: Sensitivity Tuning





- Test conditions: 30°C, ambient pressure, 500sccm flowrate, identical reference electrodes
- Previous Slide: **Pumping Current: ~0.0045 A** (Ultra-low Pt loadings with 10M H_2PO_4)
- <u>Modified [H_2PO_4] and Pt loading</u>
- **Left graph:** Varying local [H_2PO_4] significantly changes membrane conductivity (HFR).
- **Right graph:** Pumping Current is influenced by both [H_2PO_4] and Pt loading

Successfully varied the HCD pumping current!!!

Summary

- HCD improved in several iterations
  - Component modification to stabilize membrane hydration
  - Ionomer content varied for baseline stability and improved conditioning
  - Clean up strategy implemented to reset analyzer
- Sensitivity to 200ppb CO in dry H_2 has been demonstrated
- Patent filed for technology
- Field trials location identified, system installed and tested
- Less expensive Gen 2 electronics development after proven field trials testing
- Inline HCD(PBI-based) shows promise but has challenges with sensitivity

Acknowledgements

- Our funding source:
  - Laura Hill (Technology Manager, DOE HFTO)
- Collaborators:
  - H2Frontier (Burbank, CA)
  - SKYRE (Formerly Sustainable Innovations)
  - NREL, Bill Buttner
  - VI Control Systems of Los Alamos
- And the Audience!!!

Thank you